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STUDIES ON LOW-TEMPERATURE LIGNITE TAR  
IV. STUDY OF HIGH-BOILING TAR ACIDS

by

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Introduction

The purpose of the present work was to obtain enough insight about the constitution of the high-boiling tar acids that the merits of various possible industrial outlets might be properly considered. It was desired to demonstrate the presence of various molecular types in specific vacuum-distillation fractions, and where possible, to make a logical estimate of the proportion in which these types were present.

Summary

Adsorption chromatography paper and gas partition chromatography, nonaqueous titrations to determine average equivalent weights, infrared spectroscopy, mass spectroscopy, and certain specific color reactions to identify classes of tar acids were all used in this study. The types of compounds identified by these techniques are shown in Table 1. No one class of tar acids was predominant, but the presence of the various classes of compounds varied with the boiling range being studied. In general it may be said that the alkyl side chains appeared to consist primarily of methyl and ethyl groups.

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TABLE 1. CLASSES OF COMPOUNDS IDENTIFIED IN HIGH-BOILING TAR ACIDS

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|--------------------------------------------------------------------------------------------------------------------|
| (1) Alkylphenols with the total number of alkyl carbon atoms being from 3 to 6                                     |
| (2) Catechol, resorcinol, and hydroquinone and their alkylated derivatives                                         |
| (3) Trihydric phenols (probably a small quantity)                                                                  |
| (4) Indanols and alkylated indanols                                                                                |
| (5) Naphthols and alkylated naphthols                                                                              |
| (6) Higher molecular weight polynuclear phenols                                                                    |
| (7) Ketones (appeared in all 18 distillation fractions of high-boiling tar acids)                                  |
| (8) Indenols and acenaphthols were tentatively identified by mass spectrography in addition to classes noted above |
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### Experimental and Discussion

#### Preparation and Preliminary Examination of Tar-Acid-Fractions

A broad cut of crude tar acids was obtained from vacuum-flash distillate of primary tar by caustic extraction. The crude tar acids were distilled under vacuum, and a rough cut (bp 200-335 C/1 atm) was collected for subsequent study. This cut was fractionated at reduced pressure through a 65 x 2.5-cm OD column packed with 1/8-inch glass helices. Atmospheric boiling points at vigorous reflux and refractive indices of the collected fractions are shown in the left-hand portion of Figure 1. The right-hand portion of Figure 1 indicates the results of titrations for carbonylic content by the use of hydroxylamine hydrochloride.<sup>(1)\*</sup> This was attempted after qualitative infrared scanning indicated the presence of carbonylic components. The figures for weight per cent of carbonylic compound were calculated with the aid of molecular-weight approximations based on nitrogen analyses of 2,4-dinitrophenylhydrazones. The presence of compounds which are probably not phenols and possess the carbonyl function was unexpected since the precaution was taken of cross extracting the caustic solution of tar acids during their isolation.

Equivalent weights of the various fractions as shown in the right-hand portion of Figure 1 were determined by nonaqueous titration with sodium methoxide in pyridine<sup>(2)</sup> and have been corrected for content of carbonylic compounds.

\*References are located at the end of this paper.

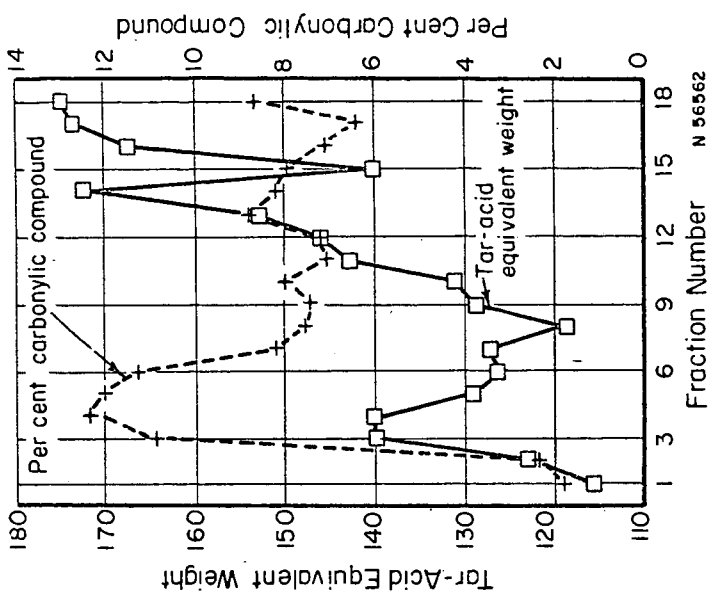
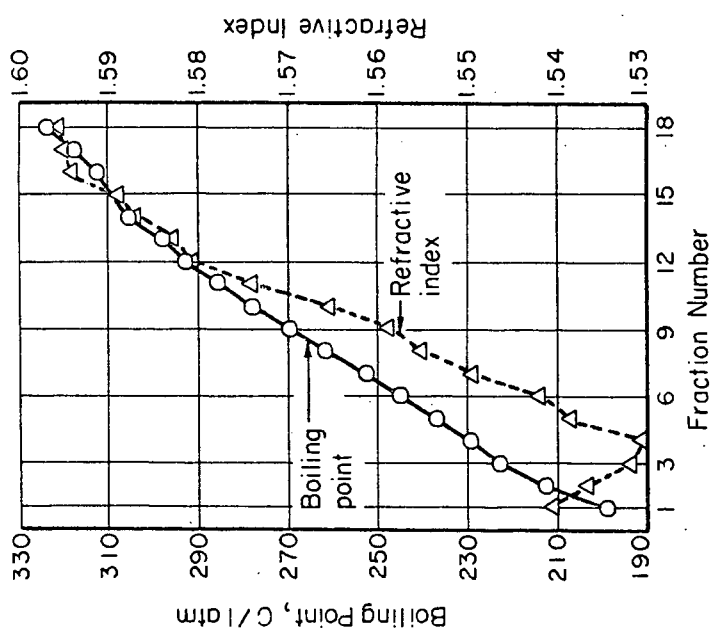


FIGURE I. PROPERTIES OF DISTILLATION FRACTIONS OF HIGH BOILING TAR ACIDS

The tar acid equivalent weights, shown in Figure 1, indicate that the content of dihydric phenols varied with the boiling range, but probably their proportion never exceeded one-fifth of the tar acids in any given boiling range.

It may be noted that tar-acid equivalent weights were reflected to some degree in changes in the refractive indices as presumably were also changes in content of alkyl side chains and concentration of polynuclear phenols.

Tests were made with 2,4,7-trinitrofluorenone reagent<sup>(3,4)</sup> to determine whether appreciable quantities of polynuclear phenols were present in specific distillation fractions. Only a slight positive test was obtained for Fractions 7 through 9; however, Fractions 10 through 18 gave a strongly positive test for polynuclear phenols.

In order to determine the presence of hydro-polynuclear phenols, dehydrogenation experiments combined with ultraviolet characterization of the products were attempted. The method worked well with known compounds, but no dehydrogenation was obtained with Fraction 12, either because the palladium catalyst had been poisoned by sulfur compounds or because no significant amount of hydro-polynuclear phenols was present.

#### Chromatography of Tar-Acid Fractions

Column and partition chromatography were also used in this investigation. Both of these techniques have been used previously to separate mixtures of tar acids.<sup>(5,6,7)</sup> Fraction 3 was selected to determine a procedure, since many of the tar acids boiling in this range had already been identified as described in the previous paper of this series. Infrared examination of each cut obtained from the chromatography of rather large samples (1-10g) on a large column\* showed that, qualitatively, appreciable separation was being achieved. Moreover, the same relative degree of separation was obtained whether the tar-acid methyl ethers\*\* were chromatographed on activated alumina, or the free tar acids on a silicic acid-celite mixture. In fact, a few specific compounds could be identified by characteristic infrared bands. This procedure was sufficient for this relatively low-boiling fraction, but for the higher-boiling fractions, which were more complex, it was necessary to supplement the infrared study of each cut with paper or gas partition chromatography.

First, a study was made of the column and paper chromatography of selected known phenols, both separately and in known mixtures. A one-milligram sample was developed on a 13 x 200-mm column of silicic acid

\*Sizes ranged from 1 x 35-in. to 2 x 67-in. columns.

\*\*Prepared by the method of Woolfolk, Columbia, et al., Bulletin 487, U. S. Bureau of Mines (1950), p. 34.

with 15 per cent ether-petroleum ether. The column was then extruded and streaked with alkaline permanganate solution. All classes of phenols reduce the permanganate to brown  $MnO_2$ . The column was also streaked with a 2 per cent solution of phosphomolybdic acid and exposed to ammonia vapors. It is known that catechol and hydroquinone develop a blue color before exposure to ammonia vapors, whereas all other phenols develop a blue color after exposure to ammonia vapors.<sup>(8)</sup> The band positions in millimeters from the top of the adsorbent are shown in Table 2. It can be seen that a reasonable separation was achieved. Various classes of phenols could be identified from synthetic mixtures.

Known phenols were developed by the ascending method with a benzene-acetic acid-water mixture on a strip of Whatman No. 1 filter paper. This developer is known to separate dihydric phenols easily from alkyl phenols.<sup>(7)</sup> An excellent separation could be achieved, and here identification of individual phenols could be made from synthetic mixtures as shown for three phenols in Table 3. Further, the relative concentration and the amount of substitution of each phenol could be estimated. After these preliminaries, a detailed study of Fractions 6 and 12 was undertaken. Where applicable the same techniques were used for other fractions.

#### Study of Fraction 6 Tar Acids

Fraction 6 of the tar acids was chromatographed on a large silicic acid-celite column and developed gradiently with ether-petroleum ether mixtures. Each of the 300, 10-ml cuts was tested with the phosphomolybdic reagent and ammonia. Dihydric phenols were found in Cuts 176-300. For further study, these cuts were combined systematically into four composites. Table 4 shows the results of the study of each of the composites.

It is known that ortho and para dihydric phenols reduce ammoniacal silver nitrate solution, whereas meta dihydric phenols do not.<sup>(8)</sup> When each composite was tested with this reagent, Composite 3 gave a very faint test and Composite 4 a strongly positive test.

Infrared examination showed that, although each composite was complex, some information relative to compound types could be obtained. For example, it could be shown that the first two composites were structurally similar. They were predominantly alkyl phenols with 4 to 6 side-chain carbon atoms consisting mainly of methyl and ethyl groups. Composite 2 showed less aliphatic CH absorption and had three absorption bands corresponding to 5-indanol. The first three composites all showed a carbonyl contaminant, estimated at about 10 per cent. Composite 4 showed very little aliphatic CH absorption, probably less than an average of two carbon atoms per ring. The aromatic position bands showed 3 or 4 adjacent ring hydrogen atoms, indicating catechol derivatives.

TABLE 2. CHROMATOGRAPHY OF KNOWN PHENOLS ON SILICIC ACID

Phenol	Band Position, mm
Hydroquinone	0-10
Hexylresorcinol	2-8
Catechol	8-20
$\beta$ -Naphthol	30-55
p-Phenylphenol	45-65
5-Indanol	60-90
p-t-Butylphenol	70-100
Octylphenol	95-120

TABLE 3.  $R_f$  VALUES FROM PAPER CHROMATOGRAPHY OF KNOWN PHENOLS WITH BENZENE-ACETIC ACID-WATER (3:3:1)

Phenol	$R_f$ Values	
	Literature <sup>(7)</sup>	Found
Hydroquinone	0.12	0.12
Resorcinol	0.13	--
Catechol	0.36	0.33
4-Methylcatechol	0.46	--
4,5-Dimethylcatechol	0.52	--
3-Methylcatechol	0.60	--
3,4-Dimethylcatechol	0.71	--
3,5-Dimethylcatechol	0.71	--
3-Ethylcatechol	0.80	--
5-Indanol	0.99	0.94
Alkylmonohydric phenols	About 0.99	--

TABLE 4. CHARACTER OF COMPOSITES OF CUTS OBTAINED FROM CHROMATOGRAPHY OF FRACTION 6 ON SILICIC ACID - CELITE

Composite	Cuts	Wt. % Recovered <sup>(a)</sup>	Refractive Index	Ammoniacal AgNO <sub>3</sub> Test	Phosphomolybdic Acid Test		Conclusions
					Before NH <sub>3</sub>	After NH <sub>3</sub>	
1	51-86 <sup>(b)</sup>	48	1.5351	--	--	+	Alkylphenols, indanols, <u>no</u> dihydric phenols
2	87-98	10	1.5472	--	--	+	Same as above, more indanols
3	97-175	21	--	Faintly +	--	+	Alkylphenols and indanols, some dihydric phenols
4	176-319	22	--	+	+	+	Highly substituted mostly dihydric phenols

(a) Over-all recovery. 75 per cent.

(b) The first 50 cuts were only solvent.

TABLE 5. PAPER CHROMATOGRAPHY OF COMPOSITE CUTS OF CHROMATOGRAPHED FRACTION 6 TAR ACIDS

Composite	R <sub>f</sub> Value	Intensity Size Factor	Remarks
1	All on solvent front	--	Alkyl phenols and indanols; no dihydric phenols
2	All on solvent front	--	Same as above
3	0.53	1	Predominantly alkyl phenols and indanols, possibly some substituted catechols
	0.73	1	
	0.81	3	
	0.97	9	
4	0.12	<1	Predominantly catechol and substituted catechols. Small amount of alkyl phenols and/or indanols.
	0.33	4	
	0.45	3	
	0.58	6	
	0.83	2	
	0.97	1	

Table 5 shows the results of paper chromatography of each composite. The intensity-size factor of each spot was a visual estimation and was an indication of concentration. The results of this study confirm the conclusions drawn from infrared examination.

#### Study of Fraction 12 Tar Acids

Fraction 12 was so complex that even the procedure followed for Fraction 6 was not satisfactory. In place of the paper chromatography, gas chromatography was used. A sample of Fraction 12 tar acids was methylated as quantitatively as possible and chromatographed on activated alumina, developing gradiently with ether-pentane mixtures. Then, 10 to 20-microliter samples of selected cuts were gas chromatographed\* and separate cuts were collected. Figure 2 shows the chromatogram and the degree of resolution obtained. Infrared examination of each of the cuts from the gas chromatographic separation showed that indeed a good separation was effected. Most of the cuts were simple mixtures composed of only a few compounds. In fact, Cut 7 was found to be pure 2-methoxynaphthalene. If more reference spectra of methyl ethers of phenols, naphthols, and indanols had been available many more compounds might have been identified.

Table 6 shows a summary of the fractions of tar acids and the information that we can give about them at this time. Upon long standing, Fractions 12, 13, 14, deposited up to 6 per cent of the same solid material. From paper chromatography and infrared study, this solid material appeared to be a pure alkyl-substituted dihydric phenol, such as a substituted hydroquinone.

#### Mass Spectroscopy of Tar Acids in Methanol Solubles

A sample of methanol solubles was supplied to Dr. Irving Wender of the U. S. Bureau of Mines at Bruceton, Pennsylvania. This material was analyzed by mass spectroscopy using a low ionization voltage to suppress all but the major peaks. Table 7 summarizes the spectrogram obtained with relative peak heights at the highest sensitivity. No effort was made to assign quantitative values to the various mass numbers as standards were not run. These data support the evidence obtained in the work just described, and it is evident that a large number of homologues are present for each tar-acid nucleus. The series of tar acids that fit the indenol and acenaphthol families are of interest, as these were not identified in the chromatographic work. Dr. Wender also obtained spectrograms for the trimethyl silyl ethers of the methanol solubles and obtained much the same pattern except the whole series was shifted to higher masses.

\*A modified Recco Distillograph Model D-2000. Research Equipment Corporation, Oakland, California.  
Runs were done at 230 C on a 10-foot column of crushed firebrick coated with Apiezon N grease.



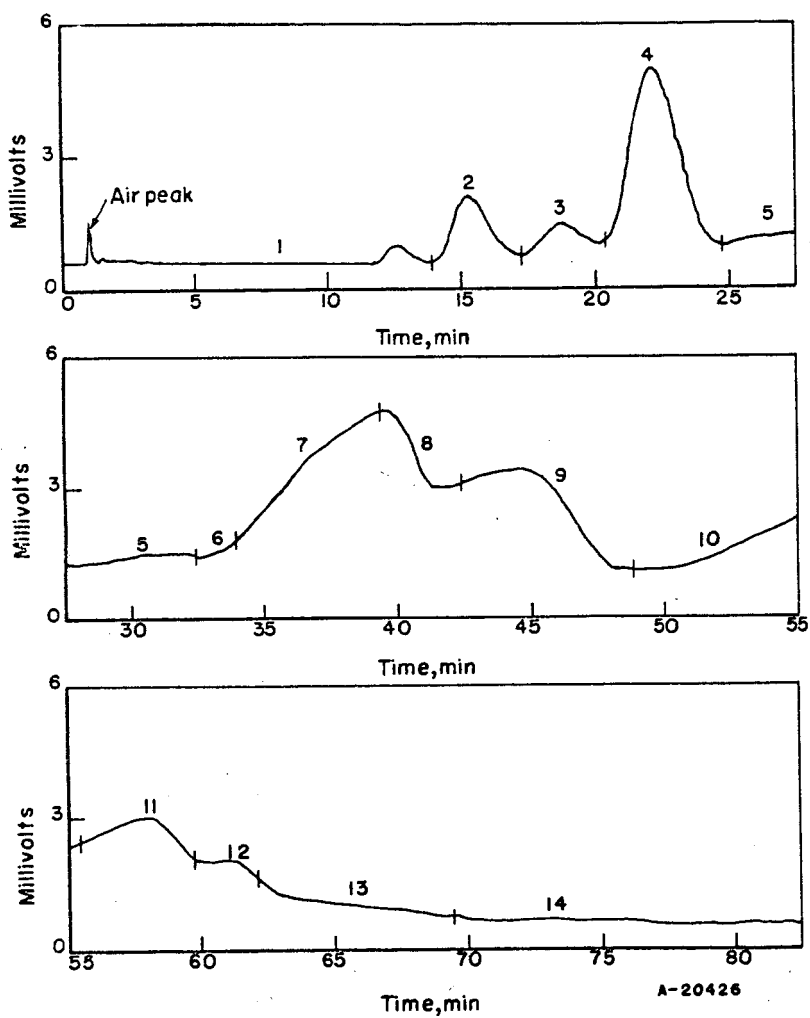

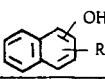

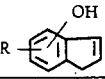
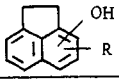



FIGURE 2. GAS CHROMATOGRAM OF CUT 5 FROM CHROMATOGRAPHY OF FRACTION B-12 TAR ACID METHYL ETHERS ON ALUMINA

TABLE 6. SUMMARY OF INFORMATION ABOUT FRACTIONS OF HIGH-BOILING TAR ACIDS

Fraction	Approx. B. P.	Equiv. Wt. of Phenols	Remarks
1	199	116	C <sub>1</sub> -C <sub>2</sub> alkylphenols
2	213	123	C <sub>1</sub> -C <sub>3</sub> alkylphenols
3	223	140	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> alkylphenols
4	229	140	C <sub>3</sub> -C <sub>4</sub> alkylphenols; traces of catechols
5	237	129	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> alkylphenols; traces of indanols; catechols and/or substituted catechols, 22 per cent
6	245	126	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> alkylphenols; indanols; catechols and substituted catechols, about one-fifth of the fraction
7	253	127	Similar to Fraction 6, possibly more indanols and substituted catechols
8	262	117	More substituted catechols; traces of resorcinol
9	269	129	Highly substituted catechols; traces of resorcinols
10	278	131	Similar to 9; about 20 per cent dihydric phenols, some substituted resorcinols; traces of polynuclear phenols
11	286	143	Traces hydroquinone; possibly polynuclear phenols
12	293	146	2 per cent solid material, probably a substituted hydroquinone; no evidence for hydrogenated polynuclear phenols; definitely polynuclear phenols
13	298	153	6 per cent of same solid as 12; polynuclear phenols
14	305	172	4 per cent of same solid as 12; low dihydric content; polynuclear phenols
15	--	157	Dihydric polynuclear phenols or trihydric alkylphenols
16	312	167	Polynuclear phenols
17	318	174	Polynuclear phenols
18	324	175	Polynuclear phenols

TABLE 7. MASS SPECTROGRAPH OF TAR ACIDS IN METHANOL SOLUBLES

Relative Peak Heights for Indicated Tar Acids <sup>(a)</sup>						
R						
H	34	7	9	5.5	1.7	5.0
C <sub>1</sub>	71	17	16	13.8	3.2	4.2
C <sub>2</sub>	60	17.5	18.6	15	3.2	4.1
C <sub>3</sub>	29	3.4	14.1	8.6	2.0	3.1
C <sub>4</sub>	9	2.3	7	3.8		1.7
C <sub>5</sub>	5.2	1.0	2.4	1.4		
C <sub>6</sub>	4.0		1.0	1.2		
C <sub>7</sub>	2.5			1.0		
C <sub>8</sub>	1.0					

(a) Peak heights below a value of 1.0 are not noted.

#### ACKNOWLEDGMENT

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